

Short remarks on the so-called fluctuation theorems and related statements

Yuriy E. Kuzovlev*

Donetsk Physics and Technology Institute, 83114 Donetsk, Ukraine

It is demonstrated that the “generalized fluctuation-dissipation theorem” [Physica A 106, 443 (1981)] covers the later suggested “fluctuation theorems” and related statistical equalities.

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1 The field of science I will talk about is the Hamiltonian statistical mechanics, that is statistical mechanics of physical systems whose all parts, - including thermostats (!), - can be described, after a suitable (canonical) choice of independent variables, by Hamilton equations or equivalent Liouville equation for probability measures in the system’s phase space (or, in quantum case, the von Neumann equation for system’s density matrix). In this field, as far as I know, statistical relations like what are presently termed “fluctuation theorems” (or “work fluctuation theorems”, etc.) for the first time were derived by G. Bochkov and me in [1–3]. They were named [3] “nonlinear fluctuation-dissipation relations” (FDR) or “generalized fluctuation-dissipation theorems”.

Simultaneously in [1–8, 21, 22] and later in [9–18] we demonstrated possibilities of their applications to

- * construction of such Markovian models of noise, relaxation, transport, and fluctuations in non-equilibrium steady states, what agree with all the FDR and consequently are thermodynamically correct [1–6, 22];

- * canonic construction of kinetic potentials and variational principles for non-equilibrium thermodynamics [4, 8, 21];

- * derivation of various particular relations between non-linear responses, fluctuations of responses and higher-order statistical characteristics of noise [1, 2, 7, 10, 22] (for example, between nonlinear optical susceptibilities and fluctuations of Raman scattering in transparent media [22]);

- * analysis of phase volume exchange and non-linear reciprocity relations between different channels of transport and dissipation [10];

- * revealing connections between statistics of transport processes (e.g. counting statistics of charge transfer) and a shape of dissipative non-linearity (e.g. CVC) [2, 3, 8, 10, 16, 22];

- * description of continuous quantum measurements and construction of formally exact stochastic evolution (Liouville) equations for open systems [15, 16];

- * construction of formally exact Langevin equations for open systems [16];

- * analysis of fluctuations in work, dissipation, relaxation and transport rates, and entropy production, in systems driven by dynamical forces (entering the system’s Hamiltonian) or/and thermic forces (entering system’s initial probability distribution) [1–3, 9, 11–13];

- * revealing and description of fundamental scaleless low-frequency (1/f-type) fluctuations in rates of irreversible processes, in particular, in mobilities and diffusivities of charge carriers and fluid molecules [9, 11–14, 17–19].

Some of the above references may supplement the G. Crooks’ [23] and later [24, 25] bibliographies on the “fluctuation theorems” and related statements.

A part of the works enumerated in these bibliographies deals with not only Hamiltonian dynamics but also with systems represented by Markovian random processes, as in [26], may be, degenerating into deterministic dissipative processes directed by non-physical toy (zero-temperature, phase volume eating) thermostats, as in [27]. Validity of “fluctuation theorems” in such model systems is not surprising, because of the above mentioned reproducibility of FDR in properly constructed Markovian models [29].

The really new things, in comparison with [1–3], are, for the first look, such relations as the “Crooks fluctuation theorem” [23–26] and the “Jarzynski equality” [24, 25, 28] which visually are significantly different from similar relations of [1–3]. Sometimes one can read that the latter are “more limited” (or “less general”, etc.) than the former. However, this is wrong opinion (perhaps, caused by laziness of thinking), and below I will demonstrate its falseness.

2. Let us consider a Hamiltonian system disturbed by some external forces $x = x(t)$ entering its Hamiltonian $H = H(x(t), \Gamma)$, where Γ denotes a full set of (canonic) variables of the system. Anyway, a character of reaction of the system to constant forces, $x = \text{const}$, is of principal importance. In one case, sufficiently weak constant forces lead to proportionally weak stable changes in the system’s state. In the opposite case, arbitrary weak constant forces can induce with time some finite or even arbitrary strong changes (the examples are responses of an isolator and a conductor to external electric field).

In [1–3], the second case was in the centre of attention. At that, clearly, it is reasonable to write

$$\begin{aligned} H(x, \Gamma) &= H_0(\Gamma) - h(x, \Gamma) , \\ h(x, \Gamma) &= x \cdot Q(\Gamma) , \end{aligned} \quad (1)$$

with quite unambiguous division of the Hamiltonian into main unperturbed part, H_0 , and its perturbation, h .

But the first case also was foreseen in [1] and [3]. At that, however, separation of main and perturbed parts of Hamiltonian no longer is unambiguous. Therefore we can write

$$\begin{aligned} H(x, \Gamma) &= H_0(\Gamma) - h(x, \Gamma) , \\ H_0(\Gamma) &= H(x_0, \Gamma) , \\ h(x, \Gamma) &= H(x_0, \Gamma) - H(x, \Gamma) , \end{aligned} \quad (2)$$

with some formally arbitrary x_0 .

Since, evidently, both the ‘‘Crooks fluctuation theorem’’ and ‘‘Jarzynski equality’’ presume just such case, we will exploit the arbitrariness of x_0 . Concretely, considering change of the external forces from $x(0)$ to $x(\theta)$ during time interval $0 < t < \theta$, let us choose

$$x_0 = x(\theta) , \quad (3)$$

and then choose the initial probability distribution to be, as in [1],

$$\rho_0(\Gamma) = \rho(x_0, \Gamma) \equiv \exp \{ \beta [F(x_0) - H(x_0, \Gamma)] \} ,$$

where

$$\exp \{ -\beta F(x) \} \equiv \int \exp \{ -\beta H(x, \Gamma) \} d\Gamma$$

This is equilibrium distribution formed before $t = 0$ under constant forces x_0 . It, however, becomes non-equilibrium after instant jump of the external forces from x_0 to $x(0)$. According to [1, 3], the exact identity takes place,

$$\begin{aligned} \langle \exp(-\beta E) \rangle &\equiv \\ &\equiv \int \exp[-\beta E(\theta, \Gamma)] \rho(x_0, \Gamma) d\Gamma = 1 , \end{aligned} \quad (4)$$

where [1]

$$\begin{aligned} E &= E(\theta, \Gamma) \equiv H_0(\Gamma(\theta)) - H_0(\Gamma) = \\ &= \int_0^\theta \left[\frac{d}{dt} - \frac{dx(t)}{dt} \cdot \frac{\partial}{\partial x(t)} \right] h(x(t), \Gamma(t)) dt = \\ &= \int_0^\theta \frac{d\Gamma(t)}{dt} \cdot \frac{\partial}{\partial \Gamma(t)} h(x(t), \Gamma(t)) dt , \end{aligned} \quad (5)$$

with $\Gamma(t)$ representing the system’s state at time t considered as the function of initial state Γ (and, of course, a functional of the forces $x(t)$).

Formally, this is trivial consequence of the phase volume conservation. Physically, since both the initial state at $t = 0$ and final state at $t = \theta$ correspond to the same values x_0 , we can treat the latter as reference point for the forces and interpret (5) as the energy dissipated by the system during its perturbation $x(t) - x_0$.

Now, let us rewrite the expression in the exponent in (4) as follows:

$$\begin{aligned} F(x_0) - E(\theta, \Gamma) - H_0(\Gamma) &= \\ &= F(x_0) - [H(x(\theta), \Gamma(\theta)) - H(x(0), \Gamma)] - H(x(0), \Gamma) , \end{aligned}$$

and the Eq.4, correspondingly, in the form

$$\begin{aligned} &\exp \{ \beta [F(x(\theta)) - F(x(0))] \} \times \\ &\times \int \exp[-\beta \mathcal{E}(\theta, \Gamma)] \rho(x(0), \Gamma) d\Gamma = \\ &= \exp \{ \beta [F(x(\theta)) - F(x(0))] \} \times \\ &\times \langle \exp[-\beta \mathcal{E}] \rangle = 1 , \end{aligned} \quad (6)$$

where

$$\begin{aligned} \mathcal{E} &= \mathcal{E}(\theta, \Gamma) \equiv H(x(\theta), \Gamma(\theta)) - H(x(0), \Gamma) = \\ &= \int_0^\theta \frac{dx(t)}{dt} \cdot \frac{\partial H(x(t), \Gamma(t))}{\partial x(t)} dt \end{aligned} \quad (7)$$

is full change of energy of the system, - consisting of changes in internal energy (i.e. dissipation) and energy of interaction with external forces, - under the same time variation of the forces as in Eq.4 [30]. Obviously, Eq.6 is nothing but the ‘‘Jarzynski equality’’ [28]. Thus, in essence, it is particular consequence of the equalities obtained in [1] or [3].

In quite similar way one can show that general relations for probability and characteristic functionals of phase trajectories, found in [1] and [3], imply [31] the Crooks’ and other ‘‘fluctuation theorems’’ [23–26]. For instance, relations like (7) from [1] or (1) from [2] in the case (2) easy transform into

$$P(\tilde{\mathcal{T}}; \tilde{x})/P(\mathcal{T}; x) = \exp \{ \beta [\Delta F - \mathcal{E}] \} , \quad (8)$$

where \mathcal{T} means (more or less detalized) phase trajectory, the tilda means time reversion (e.g. $\tilde{x}(t) = \epsilon x(\theta - t)$), $\Delta F = F(x(\theta)) - F(x(0))$, and statistical ensemble is the same as in (6). Consequently,

$$P(-\mathcal{E}; \tilde{x})/P(\mathcal{E}; x) = \exp \{ \beta [\Delta F - \mathcal{E}] \} .$$

3. In conclusion, I should notice that quantum version of the transition from Eq.4 to Eq.6 can be formulated by exact analogy with [1, 3]. At the same time, I should admit that quantum FDR still are investigated very insufficiently, and therefore the present activity in the field of ‘‘quantum fluctuation theorems’’ [25] (see also bibliography in [23–25]) undoubtedly might produce many original results.

* kuzovlev@fti.dn.ua

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- [29] The basic FDR are insensitive to internal structure of a system under consideration, in particular, to structure of its internal thermostats.
- [30] Of course, the angle brackets in Eq.4 and Eq.6 are not one and the same operation, because symbolize statistical averages over different initial ensembles.
- [31] Notice that formally the variables $Q = Q(\Gamma)$ ($\Gamma = \{\alpha, \beta\}$), $I = I(\Gamma)$, etc., in [1–3] can include all the set Γ and besides arbitrary sets of functions of Γ (at that, of course, any of the conjugated forces may be in fact time-independent, e.g. merely equal to zero).